



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) EP 0 892 028 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:  
20.01.1999 Bulletin 1999/03

(51) Int. Cl.<sup>6</sup>: C09K 11/06, H05B 33/28

(21) Application number: 98113051.1

(22) Date of filing: 14.07.1998

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 16.07.1997 JP 191681/97  
30.07.1997 JP 204697/97

(71) Applicant:  
Seiko Epson Corporation  
Shinjuku-ku, Tokyo 163-0811 (JP)

(72) Inventors:  
• Kiguchi, Hiroshi  
Suwa-shi, Nagano-ken 392-8502 (JP)  
• Kanbe, Sadao  
Suwa-shi, Nagano-ken 392-8502 (JP)  
• Seki, Shunichi  
Suwa-shi, Nagano-ken 392-8502 (JP)

(74) Representative:  
Patentanwälte  
Dr. Soff & Zapf  
Candidplatz 15  
81543 München (DE)

(54) Composition for an organic el element and method of manufacturing the organic el element

(57) A composition for an organic EL element which can form a high precision pattern in a simple manner and in a short time and a method of manufacturing the organic EL element are disclosed. By using the composition, optimum film design and luminescence characteristic can be easily obtained, and an adjustment of a luminescence efficiency can also be easily performed. The composition for an organic EL element comprises a precursor of a conjugated organic polymer compound for forming at least one luminescent layer (106), (107), (108) having a certain color and at least one kind of fluorescent dye for changing the luminescence characteristic of the luminescent layer. The luminescent layer is made from a pattern formed by an ink-jet method. As for the precursor, a precursor of PPV, PPV derivative or the like is preferably used. Further, it is preferable that the composition for the organic EL element satisfies at least one of the conditions including a contact angle of 30 to 170 degrees with respect to a nozzle surface of a nozzle provided in a head of an ink-jet device used for the ink-jet method for discharging the composition, a viscosity of 1 to 20cp and a surface tension of 20 to 70dyne/cm.

EP 0 892 028 A2

## Description

## BACKGROUND OF THE INVENTION

## 5 Field of the Invention

The present invention relates to a composition for an electroluminescent (EL) element, and more particularly to a composition for an organic EL element, and a method of manufacturing the organic EL element.

## 10 Description of the Background Art

An organic EL element has a constitution in which a cathode and an anode are connected to the opposite sides of a solid thin film containing a fluorescent organic compound. When a voltage is applied across the electrodes, electrons and holes are injected into the thin film, and they migrate according to the generated electric field and recombine with each other. At the time, excitons are produced by the energy liberated upon the recombination, and energy (in the form of fluorescence or phosphorescence) is emitted when the excitons are returned to the ground state thereof. This phenomenon is called electroluminescence.

The characteristic of an organic EL element resides in the point that a high luminance surface emission of 100 to 100,000cd/m<sup>2</sup> is possible at a low voltage of less than about 10V. Further, since organic compounds are used, there is an unlimited possibility as to the selection of the raw materials. This is the excellent advantage of the EL element, which cannot be found in other material systems. For example, by appropriate selection of the kinds of the fluorescent materials, it is possible to provide emission of visible rays ranging from blue color to red color.

In this connection, the luminescence efficiency and the stability of the EL element which are important factors of the EL element are achieved by a luminescent layer. In the past, doping of high efficiency fluorescent dyes into the luminescent layer has been carried out in order to improve the luminescence efficiency and change the emission wavelength.

The conventional organic EL element is formed into a thin film laminated-type organic thin film EL element, in which a low molecular material (host material) is mainly used as an organic EL material so that the thin film is formed of the low molecular material. Such an organic EL material is formed by adding a fluorescent dye to a low molecular weight host material. Examples of such an EL element include an element obtained by adding a fluorescent dye such as perylene or distyrylbiphenyl to a host material such as aluminum quinolynol complex (Alq<sub>3</sub>) or distyrylbiphenyl or the like.

In order to form a thin film from such a low molecular dye compound, a vapor deposition method has been so far employed. However, it is difficult to obtain a homogeneous defect-free thin film by the vapor deposition method. Further, the vapor deposition is not an efficient method, since it takes a long time to form several organic layers by the method.

## SUMMARY OF THE INVENTION

It is an object of the present invention to provide a composition for an organic EL element and a method of manufacturing such an EL element which can perform a high precision patterning in a simple manner and in a short time, achieve an optimization of a film design and a luminescence characteristic easily, and facilitate an adjustment of a luminescence efficiency, as well as form a thin film having excellent durability.

In order to achieve such an object, the present invention is directed to a composition for an organic EL element for forming at least one luminescent layer having a certain color. The composition comprises a precursor of a conjugated organic polymer compound for forming the luminescent layer; and at least one kind of fluorescent dye for changing the luminescence characteristic of the luminescent layer. Preferably, the luminescent layer is made from a pattern of the composition which is formed by an ink-jet method. In this case, the luminescence characteristic is a maximum wavelength of light absorption, and it is preferred that the conjugated organic polymer compound includes a hole injection and transfer type material.

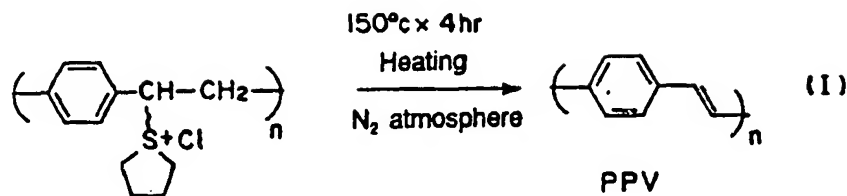
The precursor is preferably a polyallylene vinylene precursor, and more preferably a precursor of a polyparaphenylene vinylene or a polyparaphenylene vinylene derivative.

The fluorescent dye is preferably at least one selected from rhodamine or rhodamine derivative, distyrylbiphenyl or distyrylbiphenyl derivative, coumarin or coumarin derivative, tetraphenylbutadiene (TPB) or tetraphenylbutadiene derivative, and quinacridone or quinacridone derivative. In this case, the amount of the fluorescent dye to be added is preferably 0.5 to 10wt% with respect to a solid component of the precursor of the conjugated organic polymer compound.

Further, it is preferred that the precursor of the conjugated organic polymer compound and the fluorescent dye exist in the state of being dissolved or dispersed into a polar solvent. Further, it is also preferred that a wetting agent is contained in the composition.

Furthermore, it is preferred that the composition for the organic EL element satisfies at least one of the conditions

[Chemical Formula (I)]



15 Such a conjugated organic polymer compound exhibits a strong fluorescence in the solid state, and is capable of forming a homogeneous and stable solid super thin film.

Further, the conjugated organic polymer compound has an excellent formability, and has a high adhesion to an ITO electrode. In addition, such a precursor can form a sturdy conjugated polymer film after hardening. Further, since the precursor is used in the form of a precursor solution before hardening, it is possible to adjust its concentration or the like easily, thereby enabling to obtain a coating liquid suitable for ink-jet pattern formation as will be described later. This means that it is possible to set the optimum conditions for the thin film easily in a short time and to form the thin film based on the conditions.

It is preferred that the conjugated organic polymer compound is a hole injection and transfer type material. With this choice, it is possible to promote the injection and transfer of the carriers, and improve the luminescence efficiency.

25 As for example of the precursor of such a conjugated organic polymer compound, a polyallylene vinylene precursor is preferable. Since the polyallylene vinylene precursor is soluble to a water-based solvent or an organic solvent, it is possible to prepare easily the composition for the organic EL element. Further, since such a precursor can be polymerized under certain conditions, it is possible to obtain a thin film having high optical quality.

Examples of such a polyallylene vinylene precursor include: precursor of PPV derivative such as PPV (poly(para-phenylene vinylene)) precursor, MO-PPV (poly(2,5-dimethoxy-1,4-phenylene vinylene)) precursor, CN-PPV (poly(2,5-bis(hexyloxy)-1,4-phenylene-(1-cyanovinylene))) precursor, MEH-PPV (poly(2-methoxy-5-(2'-ethylhexyloxy))-para-phenylene vinylene) precursor and the like; poly(alkylthiophene) precursor such as PTV (poly(2,5-thienylene vinylene)) precursor and the like; PFV (poly(2,5-furylene vinylene)) precursor; poly(paraphenylene) precursor; and polyalkylfluorene precursor, and the like. Among these precursors, the precursor of PPV or PPV derivatives such as shown in the following chemical formula (II) is most preferable.

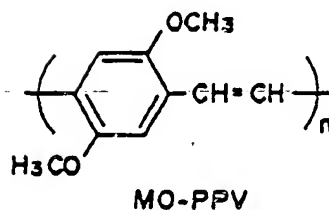
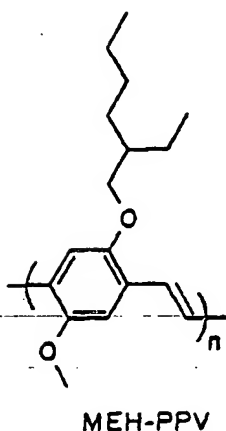
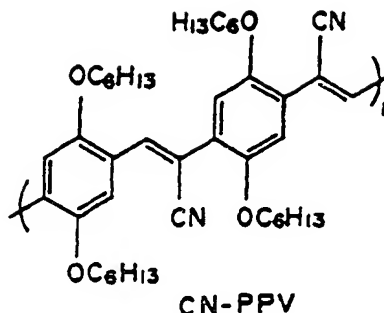
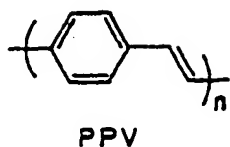
40

45

50

55

## [Chemical Formula (II)]



35

The precursor of PPV or the PPV derivative is soluble to water. After such a precursor solution is coated, heat treatment is carried out to conjugate the precursor, thereby forming a conjugated PPV thin film.

40 In the ink-jet method, it is preferable to use a composition which is soluble to water-based, alcohol-based or glycol-based solvent. Since the precursor of PPV or PPV derivative is soluble to these solvents, it is possible to avoid undesirable effect on the human body and erosion of the passage of the discharged liquid and the ink head material which would be caused when other solvent are used.

45 Further, since PPV and the like possess a strong fluorescence and it is a conductive polymer in which  $\pi$ -electron of double bond is delocalized on the polymer chain, it is possible to obtain an organic EL element having high performance.

50 The content of the precursor represented by the PPV precursor is preferably 0.01 to 10.0wt%, and more preferably 0.1 to 5.0wt%, with respect to the total amount of the composition for the organic EL element. If the amount of the precursor to be added is too small, it is insufficient for formation of the conjugated polymer film. On the other hand, if the amount of the precursor to be added is too much, the viscosity of the composition becomes high, which is not suitable for coating and pattern formation with high precision by the ink-jet method.

In addition, as for examples of polymer organic compound other than the PPV precursor which can form a luminescent layer, pyrazoline dimer, quindoline carboxylic acid, benzopyrylium perchlorate, benzopyrano quindoline, rubrene, phenanthroline europium complex and the like can be mentioned, and a composition for the organic EL element containing one of these compounds or a mixture of two or more of these compounds may also be employed.

55 Further, the composition for an organic EL element according to the present invention includes at least one kind of fluorescent dye in addition to the precursor of the conjugated organic polymer compound described above. In this way, it becomes possible to change the luminous property of the luminescent layer. Therefore, the addition of the fluorescent dye is effective as a means, for example, for improving the luminous efficiency of the luminescent layer or for changing

the maximum wavelength of light absorption (emitted color) of the luminescent layers.

Namely, a fluorescent dye can be utilized not only as a material for the luminescent layers but also as a material for the coloring matter which exhibits the luminescence function by itself. This is because almost all of the energy of the excitons which are generated by the recombination of carriers on the molecules of a conjugated organic polymer compound can be transferred onto the molecules of the fluorescent dye. In this case, the current quantum efficiency of the EL element is also increased, because the luminescence arises only from the molecules of the fluorescent dye which have a high fluorescence quantum efficiency. Accordingly, by the addition of a fluorescent dye into the composition for the organic EL element, the luminescence spectrum of the luminescent layer becomes the spectrum of the fluorescent dye, thereby enabling to change the emitted color.

In this connection, it should be noted that what is meant here by the current quantum efficiency is a scale for considering the luminescence performance according to the luminescence function, and it is defined by the following expression.

$$\eta_E = \text{energy of emitted photon} / \text{inputted electrical energy}$$

In this way, by changing the maximum wavelength of light absorption by the doping of an appropriate fluorescent dye, it becomes possible, for example, to emit the three primary colors of red, green and blue, thereby enabling to obtain a full color display device.

Further, the doping of the fluorescent dye also makes it possible to improve extremely the luminous efficiency of the organic EL element.

As for a fluorescent dye used for the red luminescent layer, laser dye DCM-1, rhodamine or a rhodamine derivative, perylene and the like are preferably used. These fluorescent dyes are soluble to solvents because they are low molecules, and have a high compatibility with PPV or the like, so that a luminescent layer with a good uniformity and good stability can be formed.

As for examples of the rhodamine derivative fluorescent dyes, rhodamine B, rhodamine B base, rhodamine 6G, and rhodamine 101 perchlorate and the like can be mentioned.

Further, as for a fluorescent dye used in the green luminescent layer, quinacridone, rubrene, DCJT and their derivatives are preferably used. Since these fluorescent dyes are low molecules in the same manner as the fluorescent dyes to be used in the above-mentioned red luminescent layer, they are soluble to solvents and have a high compatibility with PPV or the like, so that the luminescent layer can be formed.

As for the fluorescent dye used in the blue luminescent layer, distyrylbiphenyl and its derivative are preferable. These fluorescent dyes are soluble to solvents in the same manner as the above-mentioned fluorescent dyes for the red luminescent layer, and have high compatibility with PPV or the like, so that the luminescent layer can be formed.

Further, as for other fluorescent dyes for generating blue emitted color, coumarin and coumarin derivative can be mentioned. These fluorescent dyes are soluble to solvents because they are low molecules in the same manner as the above-mentioned fluorescent dyes, and have high compatibility with PPV or the like, so that the luminescent layer can be formed.

As for examples of the coumarin derivative fluorescent dyes, coumarin-1, coumarin-6, coumarin-7, coumarin 120, coumarin 138, coumarin 152, coumarin 153, coumarin 311, coumarin 314, coumarin 334, coumarin 337, coumarin 343 and the like can be mentioned.

Further, as for other fluorescent dyes (luminescent materials) for generating blue emitted color, tetraphenylbutadiene (TPB) or TPB derivative, DPVBi and the like are preferable. Since these fluorescent dyes (luminescent materials) are also low molecules, they are soluble to solvents, and have high compatibility with PPV, so that the luminescent layer can be formed.

These fluorescent dyes and luminescent materials as described above can be selectively used alone or in the form of a mixture of two or more of them.

The amount of these fluorescent dyes to be added to the solid component of the precursor of the conjugated organic polymer compound are preferably 0.5 to 10wt %, and more preferably 1.0 to 5.0wt%. If the amount of the fluorescent dye to be added is too much, it becomes difficult to maintain the weather resistance and the durability of the luminescent layer. On the other hand, the amount of the fluorescent dye to be added is too little, it is impossible to obtain sufficiently the effect of adding the fluorescent dye.

Moreover, it is preferable that the precursor and the fluorescent dye are dissolved or dispersed into a polar solvent. Since the polar solvent is capable of readily dissolving or homogeneously dispersing the precursor and the fluorescent dye, use of the polar solvent makes it possible to prevent the solid component in the organic EL composition from being stuck at the nozzle hole of ink-jet device and to prevent the nozzle hole from being clogged with the solid component. Further, it also contributes to maintain the high contact angle of the ink at the nozzle hole. In this way, it is possible to prevent the bend in the jetted direction of the ink.

As for examples of the polar solvent, water; water compatible alcohol such as methanol, ethanol and the like;

the composition with respect to the material constituting the nozzle surface increases. As a result, not only the bend in the jetted direction occurs, but also its occurrence frequency tends to increase as is discussed with reference to the case of the contact angle. On the other hand, if it exceeds 70 dyne/cm, the shape of the meniscus at the tip of the nozzle is not stable, which results in the difficulty in the control of the amount and the timings of discharge of the composition.

5 Further, as for the composition of the organic EL element of this invention, it is preferable to use a composition which has a characteristic that satisfies the above-mentioned numerical range for at least one of the characteristics including the contact angle, the viscosity and the surface tension described above. In this connection, it is more preferable to use a composition which has a characteristic that satisfies the above-mentioned numerical ranges for arbitrary combination of two characteristics, and it is most preferable to use a composition which has a characteristic that satisfies all the  
10 numerical ranges. These compositions are more suitable for the ink-jet method.

The method of manufacturing the organic EL element according to the present invention is characterized by including a step of coating a composition for the organic EL element primarily containing a precursor of a conjugated organic polymer compound by jetting out it from the nozzle hole of the head for the ink-jet device to form a pattern, and a step of forming a luminescent layer by conjugating the precursor of the conjugated organic polymer compound described  
15 above. As a composition for the organic EL element used in this method, the compositions for the organic EL element described above may be employed.

The precursor of the conjugated organic polymer compound is readily soluble to solvents, and has a large degrees of freedom in the selection for the contact angle, viscosity and surface tension of the jetting liquid. Accordingly, since it is possible to discharge an arbitrary amount of the composition to an arbitrary position, a precise pattern formation can  
20 be performed and the emission characteristics and the film properties of the luminescent layer can be easily controlled.

The method of conjugating the precursor of the conjugated organic polymer compound is not particularly limited, but it is preferable to be achieved by a heat treatment. In this way, the luminescent layer can be easily formed with a simple manner.

It is preferable that the composition for the organic EL element mainly contains a precursor of a conjugated organic polymer compound for forming a luminescent layer, and at least one kind of fluorescent dye for changing the luminescence characteristics of the luminescent layer. Since the precursor of the conjugated organic polymer compound forms a solid thin film, the fluorescent dye itself is not required to possess a thin film formation capability, so that it may be used in the form of dispersing molecules. Because of this, various fluorescent dyes can be selected widely, thereby enabling to form a desired luminescent layer.  
25

Moreover, as for the precursor of the conjugated organic polymer compound and the fluorescent dye, those compounds described in the above may be employed.  
30

The structure of the head of the ink-jet device used in the manufacturing method of the organic EL element according to the present invention is shown in Fig. 2.

The head 10 for the ink-jet device is provided with, for example, a stainless steel nozzle plate 11 and a vibration plate 13, and they are coupled via partitioning members (reservoir plates) 15.  
35

Between the nozzle plate 11 and the vibration plate 13, a liquid storage 21 and a plurality of spaces 19 are formed by means of the reservoir plates 15. The inside of the respective spaces 19 and the liquid storage 21 are filled with the composition according to the present invention, and the spaces 19 communicate with the liquid storage 21 by means of supply ports 23.

40 Further, a nozzle hole 25 is provided in the nozzle plate 11 for discharging the composition in a jet-form from the spaces 19. On the other hand, a hole 27 is formed in the vibration plate 13 for supplying the composition to the liquid storage 21.

Further, on a surface of the vibration plate 13 which is opposite to the other surface that faces with the spaces 19, piezoelectric elements 29 are attached at positions corresponding to the positions of the respective spaces 19.

45 When the piezoelectric element 29 is energized, the piezoelectric element 29 and the vibration plate 13 are deformed, by which the volume of the space 19 is changed, so that the material for the thin film is discharged from the nozzle hole 25 toward the substrate.

In this regard, it is preferable that a water repellent treatment such as Teflon coating treatment or the like are made at the inner wall portion of the nozzle hole 25 and its peripheral part in order to prevent the bend in the jetted direction  
50 of the composition and prevent clogging of the hole by the composition.

Using the head with the above construction, it is possible to form organic EL luminescent layers respectively by discharging the compositions corresponding to, for example, the three primary colors red, blue, and green according to predetermined patterns, thereby enabling to form the pixels.

According to the ink-jet method using the ink-jet device as described above, the amount of the composition to be  
55 discharged, the number of times of the discharge and the forms of patterns can be adjusted easily and handily, so that the luminescent characteristics and film thickness and the like of the luminescent layers can be controlled.

Fig. 1 is a sectional view which shows steps performed in the embodiment of the manufacturing method for an organic EL element of the present invention.

orescent dye in the green luminescent layer composition, respectively, and that glycerin of 3wt% and diethylene glycol of 12wt% were used as a wetting agent as shown in Table 5.

(Example 6)

The organic EL element was manufactured in the same way as Example 1 except that coumarin 138 was used in the blue luminescent layer composition as a fluorescent dye as shown in Table 6.

(Example 7)

The organic EL element was manufactured in the same way as Example 1 except that CN-PPV precursor which emits red color was used instead of PPV precursor and that distyrylbiphenyl of 0.0075wt% (ratio for solid portion of PPV precursor: 2wt%) was used as a blue fluorescent dye and quinaclidone of 0.0075wt % (ratio for solid portion of PPV precursor: 2wt %) was used as a green fluorescent dye without adding any red fluorescent dye, as shown in Table 7.

(Comparative Example 1)

As shown in Table 8, compositions for an organic EL element in which aluminum quinolynol complex ( $Alq_3$ ) was added as a host material and in which DCM-1 (red), TPB (blue) and coumarin 6 (green) were added as a dopant, respectively, was prepared, and then the red, green and blue luminescent layers were formed using the compositions by means of vacuum deposition method to obtain an organic EL element.

(Comparative Example 2)

As shown in Table 9, compositions for an EL element were prepared, in which aluminum quinolynol complex ( $Alq_3$ ) was added as a host material, DCM-1 (red), TPB (blue) and coumarin 6 (green) were added to the respective compositions as a dopant, and wetting agent and polar solvent were also contained. Then, respective luminescent layers were formed by the ink-jet method using the compositions in the same way as Example 1 to obtain an organic EL element.

2. Evaluation of the Luminescence Characteristics and the Film Characteristics of the Luminescent Layers

The luminescence characteristics and the film characteristics of the respective luminescent layers of the organic EL elements which were manufactured according to Examples 1 to 7 and Comparative Examples 1 and 2 described above were evaluated according to the following methods.

(1) Luminescence Starting Voltage

A prescribed voltage was applied to the element, and the applied voltage at which a luminance of 1 cd/m<sup>2</sup> is observed was defined as the luminescence starting voltage [ $V_{th}$ ].

(2) Luminescence Life

The initial luminance after a stabilization treatment has been carried out was set to 100%, and the changes in the luminance of the EL element were measured under the condition that the elements were kept in continuous luminescence by supplying a constant current of standard waveform, wherein the luminescence life is defined as the time until the luminance drops to 50% of the initial luminance.

In this case, the drive conditions for this experiment were set at 40°C for room temperature, 23% for humidity and 20 mA/cm<sup>2</sup> for current density.

(3) Luminance (Brightness)

The luminance was measured at which the current was set to 20 mA/cm<sup>2</sup>.

(4) Wavelength at Maximum Absorption

The wavelength at maximum absorption for each luminescent layer was measured,

Fig. 4 is a diagram which shows wavelength at absorption of light at the each luminescent layers of the organic EL element in Example 1. As the result of measuring the wavelength at maximum absorption for the respective lumines-

used, as shown in Table 18.

(Comparative Example 4)

- 5 The blue luminescent layer was formed in the same way as Example 8 except that coumarin 6 was used as a blue fluorescent dye instead of rhodamine B, that DMF of 75wt % was used as a polar solvent, and that no wetting agent was added, as shown in Table 19.

(Comparative Example 5)

- 10 The red luminescent layer was formed in the same way as Example 8 except that a composition which includes aqueous solution of PPV precursor of 50wt % ; glycerin of 10wt % and diethylene glycol of 10wt% for wetting agents; and DMF of 30wt% for polar solvent was used as shown in Table 20.

15 4. Evaluation of Physical Properties and Discharge Characteristic of the Composition

The contact angle, viscosity and surface tension of the compositions of Examples 8 to 13 and Comparative Examples 3 to 5 were measured.

- 20 In addition, the occurrence frequency of the bend in the jetted direction of the composition and the occurrence frequency of clogging of the nozzle hole at the time of discharging the composition from the nozzle hole of an ink-jet printer (made by EPSON Co., Ltd. Model No. MJ-500C, the material constituting the nozzle surface is a water repellent layer to which eutectic tetrafluoroethylene-nickel is plated) were also investigated

(1) Contact Angle

- 25 The contact angle for each composition with respect to the material constituting the nozzle surface was measured in accordance with the measurement method of the contact angle as stipulated in JIS K3211.

(2) Viscosity

- 30 The viscosity of each composition at 20 °C was measured using Type E viscometer.

(3) Surface Tension

- 35 For the surface tension " $\gamma$ " of each composition, the measurement was carried out by means of the drip method as follows.

- When a liquid is dripped gently from the mouth of a circular tube with flat cut plane, a droplet falls as its weight overcomes the surface tension. If the mass of the droplet is called "m", the force pulling it downward is "mg", and the force pulling it upward is  $2\pi r\gamma$  ("r" is the outer radius of the mouth of the pipe). Based on the relationship between the two forces, the surface tension " $\gamma$ " of the composition was determined by measuring "m".

(4) Occurrence Frequency of Bend in Jetted Direction

- 45 When the composition was continuously discharged (at a frequency of 7200Hz), a time required until the bend in the jetted direction occurred was measured.

(5) Occurrence Frequency of Clogging of Nozzle Hole

- 50 When the composition was continuously discharged (at a frequency of 7200Hz), a time required until the nozzle hole was leaded to be impossible to discharge the composition because of the clogging of the nozzle hole by the precipitated solid component of the composition, was measured.

The results of these experiments are shown in Table 21.

- As shown in Table 21, each of the compositions in Examples 8 to 13 has markedly lower values of the occurrence frequency of the bend in the jetted direction and the occurrence frequency of the clogging of the nozzle hole in comparison with those of Comparative Examples, and the occurrence frequencies indicated by the values were within the range of the practical level.

In particular, when all of the characteristics including the contact angle, the viscosity and the surface tension of the compositions fall within the ranges specified by this invention, the occurrence frequency of the bend in the jetted direc-



tion and the occurrence frequency of the clogging of the nozzle hole were low level, so that it was found that they were extremely excellent compositions.

In contrast, when the composition in Comparative Example 3 was discharged, the occurrence frequency of the bend in the jetted direction and the occurrence frequency of the clogging of the nozzle hole were high level since the composition of Comparative Example 3 has a tendency that the solid component in the composition is likely to stick at the periphery of the nozzle hole, so that it was found this composition can not be practically used.

The composition in Comparative Example 4 has a large value for the occurrence frequency of the bend in the jetted direction, so that it was found that it is not suitable for fine pattern formation.

Further, for the composition in Comparative Example 5, the clogging of the nozzle occurred in a short time as soon as the discharge of the composition was started, so that it could hardly discharge the composition.

## 5. Formation of Organic EL Element

Then, by carrying out a vacuum deposition of aluminum quinolynol complex to which no doping was carried out, the electron injection and transfer layer 111 having a thickness of 0.1  $\mu\text{m}$  was laminated on the luminescent layers which were formed of the respective compositions in Examples 8 to 13.

Finally, an Al - Li electrode having a thickness of 0.8  $\mu\text{m}$  was formed as the cathode 113, respectively, by the deposition method, and thereby manufacturing the organic EL elements.

## 6. Evaluation of Luminescent Characteristics and Film Properties of the Luminescent Layer

The luminescent characteristics and the film properties of the luminescent layers formed from the compositions of Examples 8 to 13 were evaluated by the same methods as described above with reference to the description "2. Evaluation of Luminescent Characteristics and Film Properties of the Luminescent Layer".

The results of these evaluations are shown in Table 22.

As can be seen from Table 22, the luminescent characteristics and the film properties of all of the luminescent layers formed using the compositions of Examples 8 to 13 were excellent. Namely, it was possible to obtain organic EL elements free from dark spots and have high luminance and long life.

In the above, the compositions for the organic EL element and the methods of manufacturing the organic EL elements have been described for respective embodiments illustrated. However, the present invention is not limited to these embodiments. Namely, in the method of manufacturing the organic EL element, it may further includes a step of inserting arbitrary intermediate layers such as a carrier transporting layer or a buffer layer between the layers. As for the buffer layer, 1,2,4-triazole (TAZ) derivative and the like can be mentioned, which is effective for improving the luminance and the luminescence life.

Further, the method may further include a step in which surface treatment such as plasma treatment, UV treatment, coupling or the like are applied to surfaces of pixel electrode, an underlying layer and the like in order to facilitate the sticking of the EL materials. Further, the method may further include a step of forming a protective layer on the cathode.

Furthermore, the material constituting the nozzle surface of the ink-jet device is not limited to those of the embodiments described above.

Moreover, in the composition for the organic EL element of the present invention, the fluorescent dye to be added for changing the luminescent characteristics is not limited to those of the embodiments as long as they can be dissolved and dispersed homogeneously into a solvent.

As described in the above, according to the compositions for the organic EL element of the present invention, a rational design of the organic EL element is possible through wide ranging selection of luminescent materials. In particular, when the composition for the organic EL element includes a precursor of a conjugated polymer based organic compound and a fluorescent dye, it is possible to manufacture an organic EL element which realizes a full color display since various kinds of luminescent layers can be obtained through the selection of various materials. In addition, it is possible to develop designs for various organic EL elements with high luminance and long life.

Further, since conditions for a composition, such as contact angle, viscosity and surface tension can be freely set, the conditions suitable as a discharge liquid for the ink-jet method can be easily adjusted.

According to the method of manufacturing the organic EL element, it is possible to employ the ink-jet method to the formation of a luminescent layer, a hole injection and transfer layer, and an electron injection and transfer layer. In that case, it is possible to carry out easily a high precise pattern formation in a short time without the occurrence of the bend in the jetted direction of a discharge liquid and the occurrence of the clogging of the nozzle hole. In addition, the optimizations of the film design and the luminescent characteristics can be readily achieved, thereby enabling to form a luminescent layer and an EL layer which are capable of easy adjustment of luminescence efficiency and have excellent durability.

Further, according to the ink-jet method, conditions such as the film thickness, the number of dots and the like can

be adjusted arbitrarily, so that the size and the pattern of the luminescent element can also be set arbitrarily.

Furthermore, according to the ink-jet method, the element can be formed without being restrained by the dimensions of the substrate and the like since the head can be moved freely. Moreover, since required amounts of materials can be arranged at required locations, it is possible to maximally exclude the uselessness of waste liquid and the like.

5 Finally, it is to be understood that the composition for the organic EL element according to the present invention is not limited to the embodiments described above, and it is possible to make various changes and additions without departing from the scope and spirit of the present invention as defined in the appended claims.

10

15

20

25

30

35

40

45

50

55

Table 1

(Example 1)

Red Luminescent Layer			Blue Luminescent Layer			Green Luminescent Layer		
Precursor	Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)	Composition	
	PPV-precursor			Precursor	PPV-precursor		Precursor	PPV-precursor
Wetting Agent	glycerin	5	10	Wetting Agent	glycerin	5	Wetting Agent	glycerin
	diethylene-glycol				diethylene-glycol			diethylene-glycol
Polar Solvent	water	1.231	23.394	Polar Solvent	water	1.231	Polar Solvent	water
	methanol				methanol			methanol
	DMF	60			DMF			DMF
Fluorescent Dye	rhodamine B	0.0075 (Ratio of Solid Portion of Precursor : 2wt%)		Fluorescent Dye	distyryl-biphenyl	0.0075 (Ratio of Solid Portion of Precursor : 2wt%)	Fluorescent Dye	Without Fluorescent Dye

Table 3

Red Luminescent Layer			Blue Luminescent Layer		Green Luminescent Layer	
Composition	Amount of Content (wt%)		Composition	Amount of Content (wt%)	Composition	Amount of Content (wt%)
Precursor	0. 3 7 5	Precursor	PPV -precursor	0. 3 7 5	Precursor	PPV -precursor
Wetting Agent	5	Wetting Agent	glycerin	5		glycerin
	1 0		diethylene -glycol	1 0		diethylene -glycol
Polar Solvent	1. 2 3 1	Polar Solvent	water	1. 2 3 1		water
	2 3. 3 9 4		methanol	2 3. 3 9 4		methanol
	6 0		DMF	6 0		DMF
Fluorescent Dye	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	distyryl -biphenyl	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	Without Fluorescent Dye

Table 4

(Example 4)

Red Luminescent Layer			Blue Luminescent Layer			Green Luminescent Layer		
Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)
Precursor	PPV-precursor	0. 3 7 5	Precursor	PPV-precursor	0. 3 7 5	Precursor	PPV-precursor	0. 3 7 5
	glycerin	3	Wetting Agent	glycerin	3	Wetting Agent	glycerin	3
	diethylene-glycol	1 2		diethylene-glycol	1 2		diethylene-glycol	1 2
Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1
	methanol	2 3. 3 9 4		methanol	2 3. 3 9 4		methanol	2 3. 3 9 4
	DMF	6 0		DMF	6 0		DMF	6 0
Fluorescent Dye	rhodamine B	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	coumarin 6	0. 0 0 3 7 5 (1 wt%)	Fluorescent Dye	Without Fluorescent Dye	—
				distyryl-biphenyl	0. 0 0 3 7 5 (1 wt%)			

Table 5

Red Luminescent Layer			Blue Luminescent Layer			Green Luminescent Layer		
Precursor	Composition		Precursor	Composition		Precursor	Composition	
	PPV-precursor	Amount of Content (wt%)		PPV-precursor	Amount of Content (wt%)		PPV-precursor	Amount of Content (wt%)
Wetting Agent	glycerin	3	Wetting Agent	glycerin	3	Wetting Agent	glycerin	3
	diethylene-glycol	12		diethylene-glycol	12		diethylene-glycol	12
Polar Solvent	water	1.231	Polar Solvent	water	1.231	Polar Solvent	water	1.231
	methanol	23.394		methanol	23.394		methanol	23.394
	DMF	60		DMF	60		DMF	60
Fluorescent Dye	rhodamine B	0.0075 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	TPB tetraphenyl-butadiene	0.0075 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	quinacridone	0.0075 (Ratio of Solid Portion of Precursor : 2 wt%)

Table 6

(Example 6)

Red Luminescent Layer			Blue Luminescent Layer		Green Luminescent Layer	
Composition		Amount of Content (wt%)	Composition	Amount of Content (wt%)	Composition	Amount of Content (wt%)
Precursor	PPV-precursor	0. 3 7 5	Precursor	PPV-precursor	Precursor	0. 3 7 5
Wetting Agent	glycerin	5	Wetting Agent	glycerin	glycerin	5
	diethylene-glycol	1 0		diethylene-glycol	diethylene-glycol	1 0
Polar Solvent	water	1. 2 3 1	Polar Solvent	water	water	1. 2 3 1
	methanol	2 3. 3 9 4		methanol	methanol	2 3. 3 9 4
	DMF	6 0		DMF	DMF	6 0
Fluorescent Dye	rhodamine B	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	coumarin 138	Fluorescent Dye	Without Fluorescent Dye
				0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)		---

Table 7

(Example 7)

Red Luminescent Layer			Blue Luminescent Layer			Green Luminescent Layer		
Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)	Composition		Amount of Content (wt%)
Precursor	CN-PPV-precursor	0. 3 7 5	Precursor	CN-PPV-precursor	0. 3 7 5	Precursor	CN-PPV-precursor	0. 3 7 5
Wetting Agent	glycerin	5	Wetting Agent	glycerin	5	Wetting Agent	glycerin	5
	diethylene-glycol	1 0		diethylene-glycol	1 0		diethylene-glycol	1 0
Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1	Polar Solvent	water	1. 2 3 1
	methanol	2 3. 3 9 4		methanol	2 3. 3 9 4		methanol	2 3. 3 9 4
	DMF	6 0		DMF	6 0		DMF	6 0
Fluorescent Dye	Without Fluorescent Dye	—	Fluorescent Dye	distyryl-biphenyl	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)	Fluorescent Dye	quinacridone	0. 0 0 7 5 (Ratio of Solid Portion of Precursor : 2 wt%)



Table 8

(Comp. Ex. 1)

Red Luminescent Layer			Blue Luminescent Layer		Green Luminescent Layer	
Host	Composition		Composition	Amount of Content (wt%)	Composition	Amount of Content (wt%)
	Alq.	Amount of Content (wt%)				
Host	Alq.	99.0	Host	Alq.	Host	Alq.
Dopant	DCM-1	1.0	Dopant	TPB	Dopant	coumarin 6
Wetting Agent	—	—	Wetting Agent	—	Wetting Agent	—
	—	—		—		—
Polar Solvent	—	—	Polar Solvent	—	Polar Solvent	—
	—	—		—		—
	—	—		—		—

Table 9

(Comp. Ex. 2)

Red Luminescent Layer			Blue Luminescent Layer		Green Luminescent Layer		
Composition		Amount of Content (wt%)	Composition		Composition		Amount of Content (wt%)
Host	Alq <sub>3</sub>	24.0	Host	Alq <sub>3</sub>	Host	Alq <sub>3</sub>	23.95
Dopant	DCM-1	1.0	Dopant	TPB	Dopant	coumarin 6	1.05
Wetting Agent	glycerin	5	Wetting Agent	glycerin	Wetting Agent	glycerin	5
	DEG	10		DEG		DEG	10
Polar Solvent	chloroform	10	Polar Solvent	chloroform	Polar Solvent	chloroform	10
	DMF	50		DMF		DMF	50

Table 10

	Luminescence Starting Voltage [V <sub>0.5</sub> ]			Luminescence Life [hr]			Luminance [cd/m <sup>2</sup> ]			Wavelength at Maximum Absorption [nm]		
	R	G	B	R	G	B	R	G	B	R	G	B
Example 1	3	3	5	5000	5000	5000	2000	2000	2000	590	530	420
Example 2	4	3	5	5000	5000	5000	2000	2000	2000	600	530	410
Example 3	4	3	6	5000	5000	5000	2000	2000	2000	620	530	420
Example 4	4	3	5	5000	5000	5000	2000	2000	2000	620	530	415
Example 5	4	3	5	5000	5000	5000	2000	2000	2000	590	525	420
Example 6	4	3	5	5000	5000	5000	2000	2000	2000	590	530	420
Example 7	4	4	5	5000	5000	5000	2000	2000	2000	620	530	430
Comp. Ex. 1	10	10	10	1000	1000	1000	1400	1200	1000	550	510	450
Comp. Ex. 2	Impossible to form pattern											

Table 11

	Stability in Film Formation		
	R	G	B
Example 1	○	○	○
Example 2	○	○	○
Example 3	○	○	○
Example 4	○	○	○
Example 5	○	○	○
Example 6	○	○	○
Example 7	○	○	○
Comp. Ex. 1	○	△	×
Comp. Ex. 2	Impossible to form pattern		

Table 12

(Example 8)

Composition	Name of Material	Amount of Content (wt%)
Precursor	aqueous solution of PPV precursor (1.5wt%) (mixed solution of water/methanol=5/95)	2.5
Wetting Agent	glycerin	5
	diethylene glycol	10
Polar Solvent	DMF (N,N-dimethyl formamide)	60
Fluorescent Dye	rhodamine B	0.0075 (Ratio of Solid Portion of Precursor 2wt%)

Table 13

(Example 9)

Composition	Name of Material	Amount of Content (wt%)
Precursor	aqueous solution of PPV precursor (1.5wt%) (mixed solution of water/methanol=5/95)	25
Wetting Agent	glycerin	5
	diethylene glycol	10
Polar Solvent	DMF (N,N-dimethyl formamide)	60
Fluorescent Dye	distyrylbiphenyl	0.0075 (Ratio of Solid Portion of Precursor 2 wt%)

Table 14

(Example 10)

Composition	Name of Material	Amount of Content (wt%)
Precursor	aqueous solution of PPV precursor (1.5wt%) (mixed solution of water/ethanol=5/95)	2.5
Wetting Agent	glycerin	5
	diethylene glycol	10
Polar Solvent	DMF (N,N-dimethyl formamide)	60
Fluorescent Dye	quinacridone	0.0075 (Ratio of Solid Portion of Precursor 2wt%)

Table 15

(Example 11)

Composition	Name of Material	Amount of Content (wt%)
Precursor	aqueous solution of PPV precursor (1.5wt%) (mixed solution of water/methanol-5/95)	2.5
Wetting Agent	glycerin	3
	diethylene glycol	1.2
Polar Solvent	DMP (N,N-dimethyl formamide)	6.0
Fluorescent Dye	coumarin 6	0.0075 (Ratio of Solid Portion of Precursor 2wt%)



Table 16

(Example 12)

Composition	Name of Material	Amount of Content (wt%)
Precursor	aqueous solution of PPV precursor (1.5wt%) (mixed solution of water/methanol-5/95)	25
Wetting Agent	glycerin	5
	diethylene glycol	10
Polar Solvent	DMF (N,N-dimethyl formamide)	60
Fluorescent Dye	TBP (tetraphenylbutadiene)	0.0075 (Ratio of Solid Portion of Precursor 2wt%)

Table 17

(Example 13)

Composition	Name of Material	Amount of Content (wt%)
Precursor	aqueous solution of CN-PPV precursor (1.5wt%)	2.5
	(mixed solution of water/methanol=5/95)	
Wetting Agent	glycerin	5
	diethylene glycol	10
Polar Solvent	DMF (N,N-dimethyl formamide)	60
Fluorescent Dye	quinacridone	0.0075 (Ratio of Solid Portion of Precursor 2wt%)

Table 18

(Comp. Ex. 3)

Composition	Name of Material	Amount of Content (wt%)
Precursor	aqueous solution of PPV precursor (1.5wt%) (mixed solution of water/methanol=5/95)	50
Wetting Agent	glycerin	20
	diethylene glycol	20
Polar Solvent	DMF (N,N-dimethyl formamide)	10
Fluorescent Dye	quinacridone	0.0075 (Ratio of Solid Portion of Precursor 1wt%)

Table 19

(Comp. Ex. 4)

Composition	Name of Material	Amount of Content (wt%)
Precursor	aqueous solution of PPV precursor (1.5wt%) (mixed solution of water/methanol=5/95)	2.5
Wetting Agent	glycerin	0
	diethylene glycol	0
Polar Solvent	DMF (N,N-dimethyl formamide)	7.5
Fluorescent Dye	coumarin 6	0.0075 (Ratio of Solid Portion of Precursor 2 wt%)

Table 20

(Comp. Ex. 5)

Composition	Name of Material	Amount of Content (wt%)
Precursor	aqueous solution of PPV precursor (1.5wt%)	5 0
	(mixed solution of water/methanol=5/95)	
Wetting Agent	glycerin	1 0
	diethylene glycol	
Polar Solvent	DMF (N,N-dimethyl formamide)	3 0
Fluorescent Dye	rhodamine B	0. 0 0 7 5 (Ratio of Solid Portion of Precursor 1 wt%)

Table 21

(Result of Experiment)

Composition	Viscosity[cp]	Surface Tension [dyne/cm]	Contact Angle[°]	Occurrence Frequency of Bend in Jetted Direction (sec)	Occurrence Frequency of Clogging (sec)
Example 8	3.72	32.9	59	3.000	more than 10.000
Example 9	3.60	30.1	60	2.800	more than 10.000
Example 10	3.62	39.6	40	2.800	more than 10.000
Example 11	2.80	31.6	38	2.900	more than 10.000
Example 12	3.58	33.2	36	3.000	9.000
Example 13	3.86	33.6	64	2.800	9.000
Comp. Ex. 3	30.3	18.5	20	100	1.000
Comp. Ex. 4	0.9	90	175	200	more than 10.000
Comp. Ex. 5	25	15	28	Impossible to discharge composition	

Table 22

	Luminescence Starting Voltage [V <sub>on</sub> ]	Luminescence Life [hr]	Luminance [cd/m <sup>2</sup> ]	Wavelength at Maximum Absorption [nm]	Stability in Film Formation
Example 8	3.0	5000	2000	620	○
Example 9	4.5	4900	1800	420	○
Example 10	4.2	4800	1700	530	○
Example 11	4.3	4900	1900	480	○
Example 12	4.0	4800	1900	430	○
Example 13	5.6	4500	1850	530	○

# Claims

1. A composition for an organic EL element for forming at least one luminescent layer having a certain color, said composition comprising;

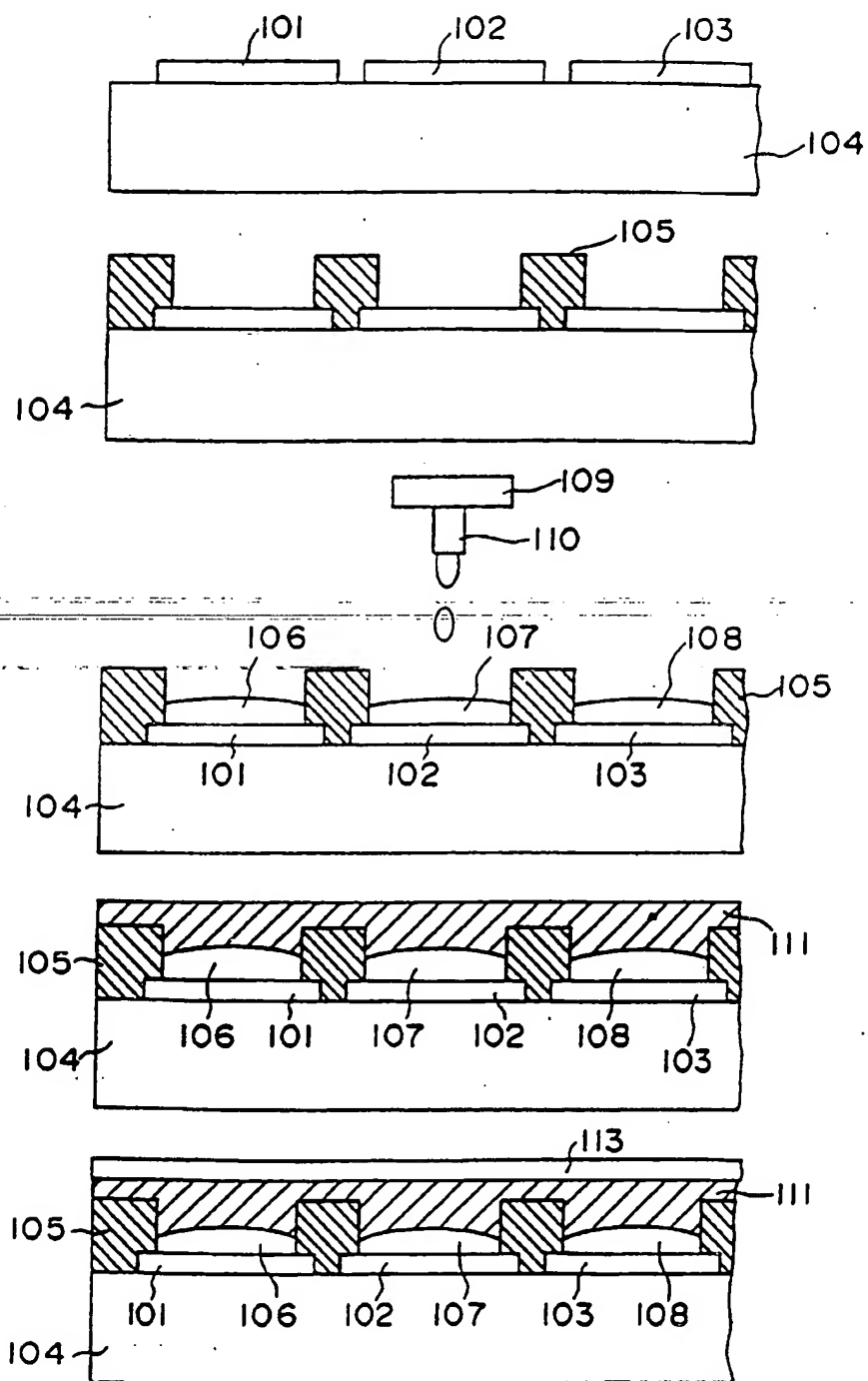
a precursor of a conjugated organic polymer compound for forming said luminescent layer; and  
at least one kind of fluorescent dye for changing the luminescence characteristic of the luminescent layer.

2. The composition for an organic EL element as claimed in claim 1, wherein said luminescent layer is formed from a pattern of the composition which is formed by an ink-jet method.
3. The composition for an organic EL element as claimed in claim 1, wherein the luminescence characteristic is a maximum wavelength of light absorption.
4. The composition for an organic EL element as claimed in claim 1, wherein the conjugated organic polymer compound is a hole injection and transfer type material.
5. The composition for an organic EL element as claimed in claim 1, wherein the precursor of the conjugated organic polymer compound includes a polyallylene vinylene precursor.
6. The composition for an organic EL element as claimed in claim 5, wherein the precursor of the conjugated organic polymer compound includes a precursor of a polyparaphenylene vinylene or a polyparaphenylene vinylene derivative.
7. The composition for an organic EL element as claimed in claim 1, wherein the fluorescent dye includes rhodamine or rhodamine derivative.
8. The composition for an organic EL element as claimed in claim 1, wherein the fluorescent dye includes distyrylbiphenyl or distyrylbiphenyl derivative.
9. The composition for an organic EL element as claimed in claim 1, wherein the fluorescent dye includes coumarin or coumarin derivative.
10. The composition for an organic EL element as claimed in claim 1, wherein the fluorescent dye includes tetraphenylbutadiene (TPB) or tetraphenylbutadiene derivative.
11. The composition for an organic EL element as claimed in claim 1, wherein the fluorescent dye includes quinacridone or quinacridone derivative.
12. The composition for an organic EL element as claimed in claim 1, wherein the precursor of the conjugated organic polymer compound and the fluorescent dye exist in the state of being dissolved or dispersed into a polar solvent.
13. The composition for an organic EL element as claimed in claim 1, wherein the amount of the fluorescent dye to be added is 0.5 to 10wt% with respect to a solid component of the precursor of the conjugated organic polymer compound.
14. The composition for an organic EL element as claimed in claim 1, wherein the composition contains a wetting agent for preventing the composition from being dried and solidified.
15. The composition for an organic EL element as claimed in claim 2, wherein a contact angle with respect to a material constituting a nozzle surface of a nozzle provided in a head of an ink-jet device used for the ink-jet method for discharging the composition lies in the range of 30 to 170 degrees.
16. The composition for the organic EL element as claimed in claim 1, wherein a viscosity of the composition for the organic EL element is 1 to 20cp.
17. The composition for the organic EL element as claimed in claim 1, wherein a surface tension of the composition for the organic EL element is 20 to 70dyne/cm.
18. A method of manufacturing an organic EL element, comprising the steps of:
  - coating a pattern by discharging a composition for an organic EL element containing a precursor of a conjugated organic polymer compound from a head by an ink-jet method; and
  - forming at least one luminescent layer for a certain color by conjugating the precursor of the conjugated organic polymer compound.



19. The method of manufacturing the organic EL element as claimed in claim 18, wherein the composition further comprises at least one kind of luminescent dye for changing a luminescence characteristic of the luminescent layer.
- 5 20. The method of manufacturing the organic EL element as claimed in claim 19, wherein the luminescence characteristic is a maximum wavelength of light absorption.
21. The method of manufacturing the organic EL element as claimed in claim 18, wherein the conjugated organic polymer compound is a hole injection and transfer type material.
- 10 22. The method of manufacturing the organic EL element as claimed in claim 18, wherein the precursor of the conjugated organic polymer compound includes a precursor of a polyallylene vinylene.
23. The method of manufacturing the organic EL element as claimed in claim 22, wherein the precursor of the polyallylene vinylene includes a precursor of a polyparaphenylene vinylene or a polyparaphenylene vinylene derivative.
- 15 24. The method of manufacturing the organic EL element as claimed in any one of claims 19, wherein the fluorescent dye includes rhodamine or rhodamine derivative.
- 25 25. The method of manufacturing the organic EL element as claimed in claim 19, wherein the fluorescent dye includes distyrylbiphenyl or distyrylbiphenyl derivative.
26. The method of manufacturing the organic EL element as claimed in claim 19, wherein the fluorescent dye includes coumarin or coumarin derivative.
27. The method of manufacturing the organic EL element as claimed in claim 19, wherein the fluorescent dye includes tetraphenylbutadiene (TPB) or tetraphenylbutadiene derivative.
28. The method of manufacturing the organic EL element as claimed in claim 19, wherein the fluorescent dye includes quinacridone or quinacridone derivative.
- 30 29. The method of manufacturing the organic EL element as claimed in claim 18, wherein a contact angle with respect to a material constituting a nozzle surface of a nozzle of a device used for the ink-jet method for discharging the composition lies in the range of 30 to 170degrees.
- 35 30. The method of manufacturing the organic EL element as claimed in claim 18, wherein a viscosity of the composition for the organic EL element is 1 to 20cp.
- 40 31. The method of manufacturing the organic EL element as claimed in 18, wherein a surface tension of the composition for the organic EL element is 20 to 70dyne/cm.

FIG. 1



**FIG. 2**

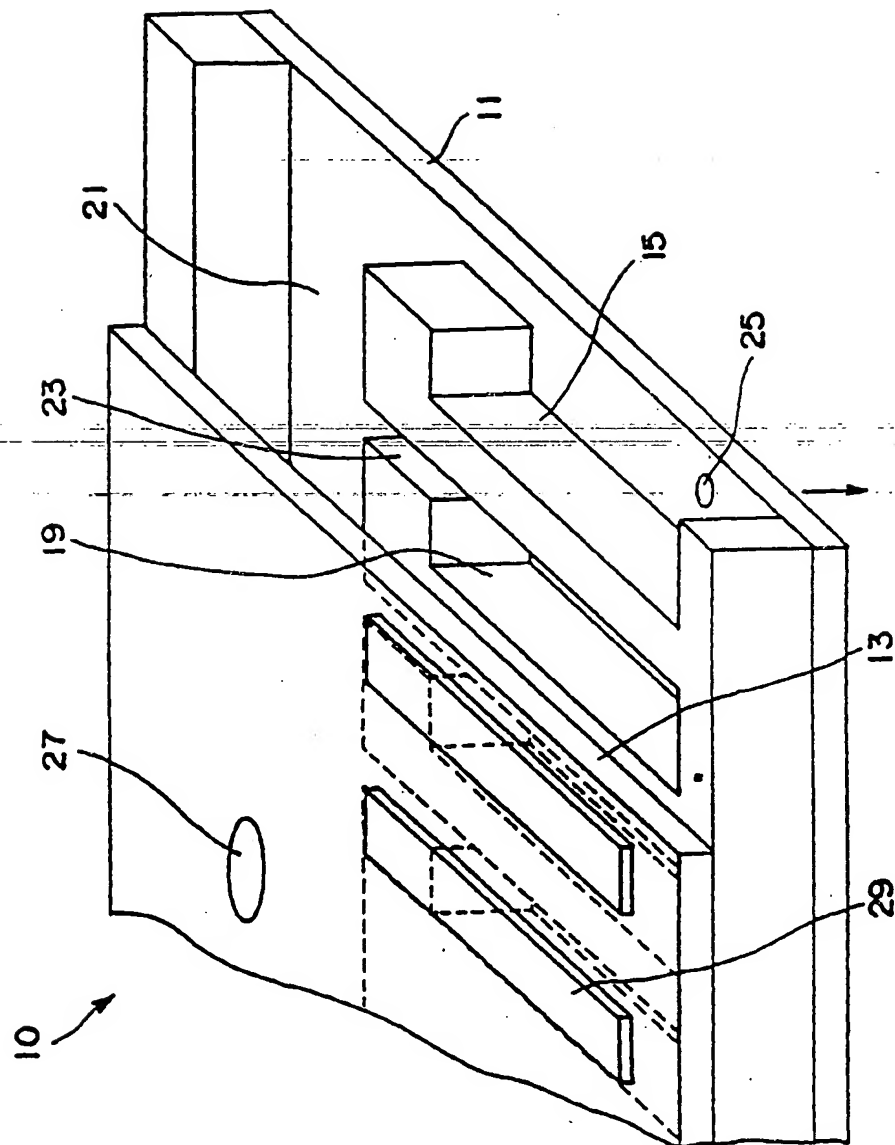


FIG. 3

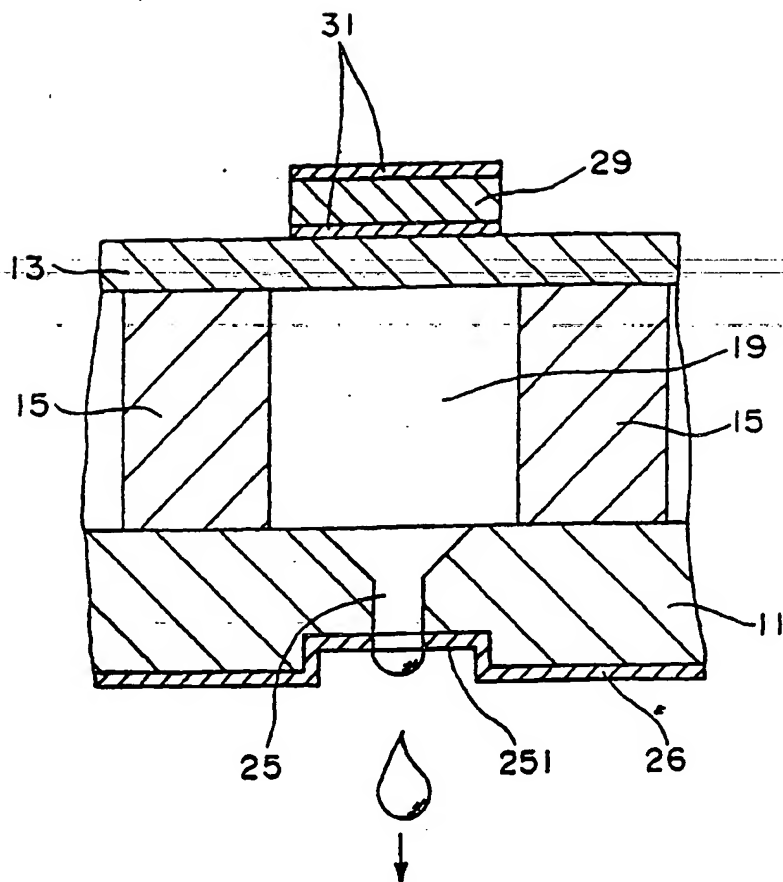


FIG. 4

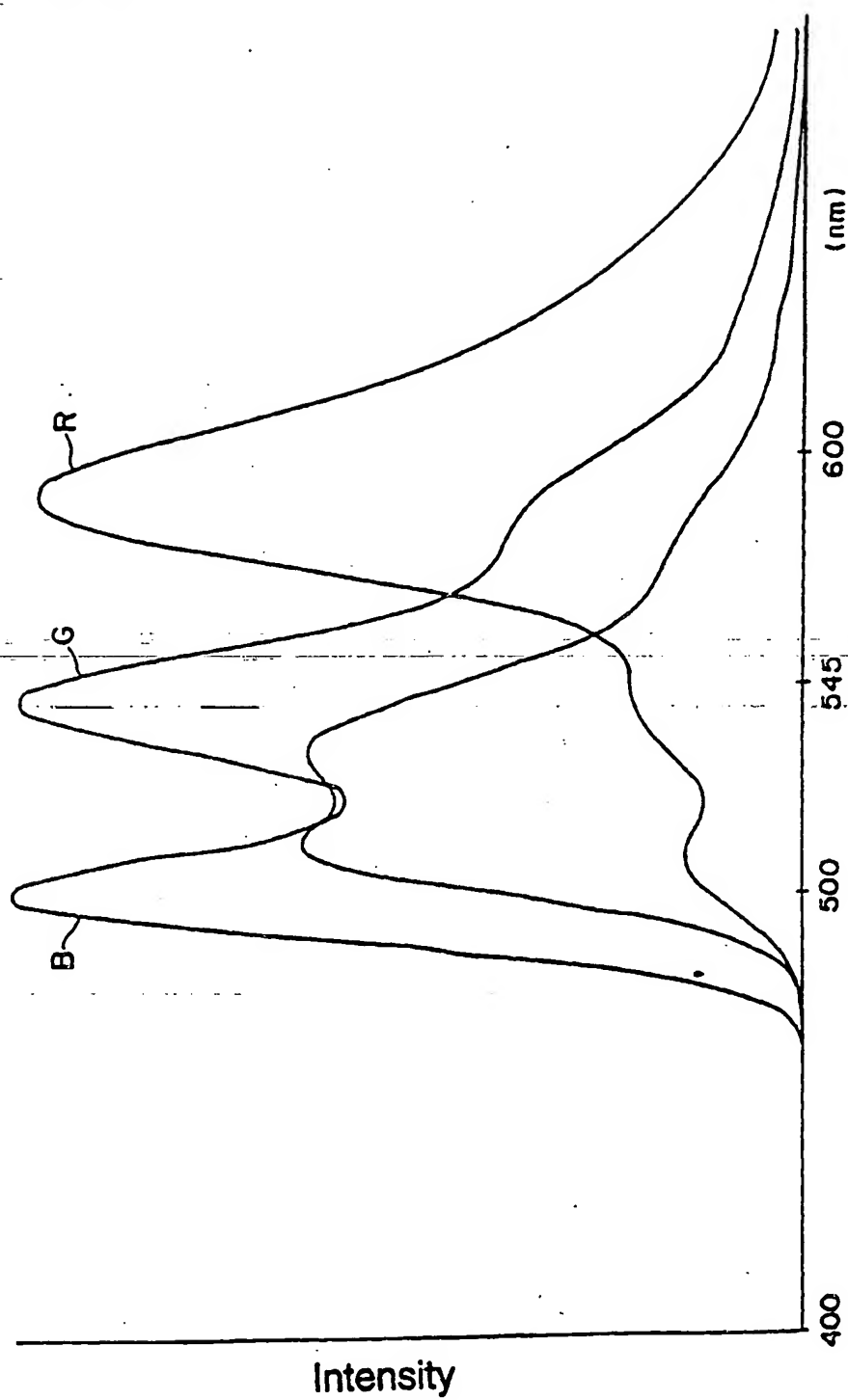


FIG. 5

